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No-Phonon $^4T_{2g}$ - $^4A_{2g}$ Transitions of Cr^{3+} in TiO$_2$

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Absorption and emission at 4 and 77 K are observed in Cr-doped TiO$_2$ consisting of two sharp no-phonon lines at 12 685 and 12 732 cm^{-1}, and vibronic sidebands with an integrated intensity 10^4 times that of the no-phonon lines. In undoped TiO$_2$, identical spectra are observed but are a factor of 100 less intense. The center responsible for these spectra is identified as substitutional Cr^{3+} by observing, in emission, a splitting of the 12 685-cm^{-1} line of 1.4 cm^{-1}, a value previously determined by EPR measurements. The vibronic sidebands have some structure superposed on a broad band. The vibronics are different in emission and absorption and have a lifetime of 45 μsec, equal to that of the no-phonon line. They are shown to be principally due to defect-induced phonons arising from the Cr^{3+} defect. We argue that the spectra observed are not characteristic of the usual ^2E_g-$^4A_{2g}$ transition, and propose that the $^4T_2$ lies lower in energy than the ^2E_g state. If so, the new results of this work are (1) no-phonon line emission for the $^4T_2$-$^4A_2$ transition and (2) defect phonon states which are different for the $^4A_2$ and $^4T_2$ states. The excitation spectrum is also presented. It shows that the excitation of the Cr^{3+} emission occurs mainly by the transfer of energy from excited trapping centers rather than by direct excitation.

I. INTRODUCTION

The motivation for the experiments to be reported in this paper was the observation, upon preliminary examination at 77 K, of sharp line photoluminescence at ~8000 Å in undoped TiO$_2$. In some ways, the fluorescence suggested similarities to that of Cr^{3+} in SrTiO$_3$ in which one of us[1] (S. S.) suggested that it is due to Cr^{3+} while the other[2] (L. G.) proposed that it is not. Later, Burke and Pressley[3] in a study of the Zeeman effect of the sharp line infrared fluorescence of SrTiO$_3$ concluded that the sharp line could be consistently interpreted as a transition from the ^2E_g state to the $^4A_{2g}$ state of Cr^{3+}. The question then arose: is the fluorescence observed in undoped TiO$_2$ due to a Cr^{3+} ion or not? This decision was facilitated by the study of Gerritsen *et al.*[4] of the electron paramagnetic resonance spectrum of Cr-doped TiO$_2$ in which the splitting of the $^4A_{2g}$ ground state of Cr^{3+} was measured to be 1.4 cm^{-1} and, therefore, easily resolved optically. In brief then, optical absorption, photoluminescence, and excitation spectra presented in this paper unequivocally decide in favor of Cr^{3+} fluorescence in TiO$_2$. Thus, just as in the case of SrTiO$_3$, spectrochemically undetectable amounts of Cr are easily detected in photoluminescence.

However, analysis of our data presented unexpected difficulties for the "standard" interpretation in which the lowest-lying electronic excited state of the Cr^{3+} is the ^2E_g state. Instead we believe that our data suggest that the $^4T_{2g}$ state is the lowest-lying electronic excited state of Cr^{3+} in TiO$_2$, and a major portion of this paper is devoted to this thesis. If our suggestion is correct, the $^4T_{2g} \rightarrow {}^4A_{2g}$ emission of Cr^{3+} in TiO$_2$ is unique in that this transition gives rise to *line emission* in addition to the usual broad-band emission. Previous work on Cr^{3+} in octahedral oxygen coordination show only a few cases[5-7] in which the lowest excited state is the $^4T_{2g}$ state rather than the ^2E_g state. In contrast to Cr^{3+} in TiO$_2$, however, the $^4T_{2g}$ zero-phonon transition was not seen.

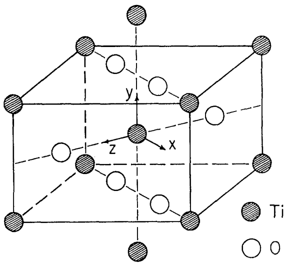

FIG. 1. Rutile structure. The y axis is the c axis of the crystal; the x and z axes are at 45° with respect to the a axes.

An additional motivation for investigating the fluorescence of Cr^{3+} in TiO$_2$ was the possibility of observing a temperature-dependent optical phonon in the vibronic spectrum. The static dielectric constant ϵ of TiO$_2$ changes with temperature,[8] and thus, according to the "soft-mode theory" of Anderson[9] and Cochran,[10] there should be a temperature-dependent transverse optic mode of vibration. Rutile has the advantage of being uniaxial, making the identification of the phonon symmetries easier through their polarization properties. However, it will be shown that the vibronic spectrum that we observe is frustrated by the dominance of defect-induced phonons, the defect being the Cr^{3+} ion. In fact, the vibronics in absorption and emission are different and are not related in an obvious way to the measured values of the phonon frequencies at the center of the Brillouin zone.[11]

Finally, the work reported here may be considered a link in the spectroscopy of transition-metal ions in the titanates that has recently become available: Zn$_2$TiO$_4$:Mn^{4+}, Mg$_2$TiO$_4$:Mn^{4+},[12] MgTiO$_3$:Mn^{4+},[13] Mg$_2$TiO$_4$:Cr^{3+},[14] SrTiO$_3$:Cr^{3+},[1-3] SrTiO$_3$:Mn^{4+},[1] and CaTiO$_3$:Cr^{3+}.[15]

The experimental technique used in this study has been described previously.[2]

II. CRYSTALS

Large single crystals of TiO$_2$ and TiO$_2$:Cr grown by the Verneuil flame fusion method were either purchased commercially or grown in this laboratory. In undoped crystals the Cr concentration was below the detection limit of emission spectrochemical analysis. Chromium-doped crystals were doped either 0.005 or 0.02% by weight. The data shown are for the best crystals only, our criterion being the linewidth of the zero-phonon line. This linewidth varied from boule to boule presumably because of strain broadening. The excitation spectra and photoconductivity spectra were found to be sensitive to the condition of the surface of the crystal in the region of band-to-band absorption (~ 3 eV). This could be eliminated by a chemical polish consisting of dipping the crystal in molten NaOH (600 C) for 1 min and subsequent cleaning in boiling concentrated HCl. The crystals were then washed in distilled water.

Parenthetically, we would like to add that an attempt to observe the Mn^{4+} fluorescence in Mn-doped TiO$_2$ was unsuccessful. From this we conclude that the state of the Mn ion is not mainly Mn^{4+}. Presumably it is Mn^{3+}. Attempts to convert the Mn^{3+} to Mn^{4+} by heating the Mn-doped TiO$_2$ in oxygen at a pressure of 10 kbar at 500 C were also unsuccessful.

The rutile form of TiO$_2$ is a tetragonal crystal belonging to the crystal class D_{4h} and the space group D_{4h}^{14} ($P4_2/mnm$). The unit cell (Fig. 1) contains six atoms. Each Ti^{4+} ion is surrounded by a slightly deformed oxygen octahedron, so that the local symmetry of a Ti^{4+} site is only orthorhombic (D_{2h}). There are two Ti sites in the unit cell, and they are related by a rotation of 90° around the c axis of the crystal. From the EPR work of Gerritsen *et al.* we know that in Cr-doped TiO$_2$ almost all the Cr^{3+} ions are in Ti^{4+} substitutional sites with no local charge compensation.

III. RESULTS AND DISCUSSION

Figure 2 shows the gross features of the optical absorption in Cr-doped TiO$_2$. The weak band at 1.7 eV, after subtraction of the "background" absorption, has a strength proportional to the Cr^{3+} concentration and is due to a d-d transition of the Cr^{3+} ion, as we shall see later. The "background" absorption in the visible part of the spectrum is not due to the Cr ion. This can be shown by heating a Cr-doped crystal of TiO$_2$ in H$_2$ at 500 C. As a result of this treatment, the absorption in the visible part of the spectrum decreased by a factor of about 5. In contrast to this the absorption around 1.7 eV, after subtraction of the "background" remained unchanged. This "background" absorption is characteristic of transition-metal-doped titanates, SrTiO$_3$ and CaTiO$_3$ doped with Cr^{3+}, Fe^{3+}, and Co^{3+}, for example. We speculate that since the "background absorption" occurs only when the crystal is doped, it arises because of defects induced by the dopant.

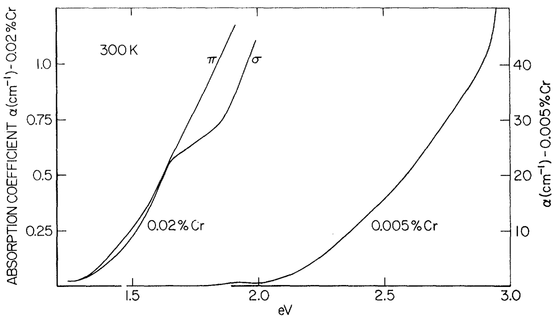

FIG. 2. Absorption of TiO$_2$:Cr^{3+} at room temperature.

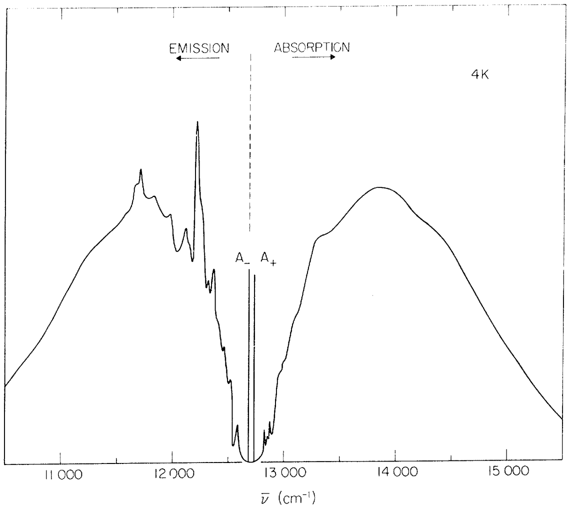

FIG. 3. Comparison of absorption and emission of the Cr^{3+} ion in TiO_2 at 4 K. A_+ and A_- are no-phonon lines.

Ghosh *et al.*[16] were first to observe a broad unsymmetrical emission band at 8500 Å in undoped TiO_2 at 77 K. In undoped TiO_2 and under low spectral resolution, we have observed the same emission band at 77 K. Under high resolution, however, we find that this emission band breaks up into a spectrum of considerable structure.

Ghosh *et al.* tentatively identified the emission center as an interstitial Ti^{3+} ion. Anticipating its identification, to be demonstrated below, we shall conclude that it is, in fact, substitutional Cr^{3+}.

The same emission occurs in TiO_2:0.005% Cr although it is about 100 times stronger. For TiO_2:0.005% Cr at 4 K the gross features of the emission are shown in Fig. 3, which also includes an absorption spectrum of a TiO_2:0.02% Cr sample. A more detailed emission spectrum at 4 and 77 K is shown in Fig. 4. Two sharp lines, henceforth to be identified as the A_- and A_+ lines, are seen in emission at 77 K. The lower energy line A_- is at 12 685 cm^{-1}; the higher energy line A_+ lies 47 cm^{-1} higher in energy. The same two sharp lines are seen in absorption. The emission and absorption spectra are unsymmetrical with respect to the sharp lines. Greater structure is seen in emission than in absorption. We also find the relative intensities of the components of the spectrum independent of Cr concentration, including a nominal doping of zero, and that the decay time of the emission line (zero-phonon line) A_- at 12 685 cm^{-1} and the broad-band emission are equal. We, therefore, conclude that the emission is caused by a single center.

The identity of the center, as Cr^{3+}, was established by observing that in emission, at 4 K the zero-phonon line A_- is split by 1.33 cm^{-1}, as shown in the inset of Fig. 4. Since the lines overlap, the true separation of the lines is about 1.4 cm^{-1}. Now Gerritsen *et al.*, using the technique of electron spin resonance, showed that Cr enters TiO_2 as Cr^{3+} by substituting for a Ti^{4+} ion, and that the splitting of the $^4A_2$ ground state is 1.44 cm^{-1}. We, therefore, conclude that the center, in our case, is also Cr^{3+}. Additional confirmation is that, as will be shown later, the zero-phonon line is a magnetic dipole transition and that, therefore, the center site is centrosymmetric, which is necessarily the case if Cr^{3+} substitutes for a Ti^{4+} ion without local charge compensation.

In this paragraph, we summarize some of the main properties of the absorption and emission spectra. The higher energy line A_+, 47 cm^{-1} from the A_- line, is absent in emission at 4 K; furthermore, its position at 77 K coincides with that in absorption at 4 K. From the fact that its linewidth is identical to that of the A_- line, we conclude that the A_+ line is, also, an electronic transition of the Cr^{3+} ion. From the temperature dependence of the intensity of the A_+ line, we find that the 47-cm^{-1} splitting is in the excited state. The lifetime of

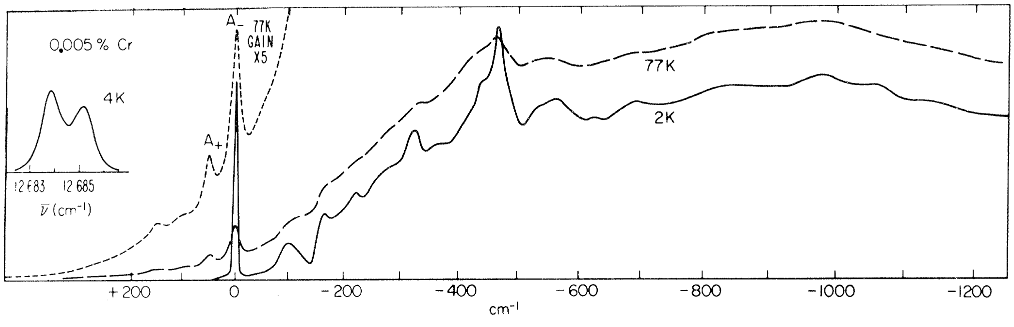

FIG. 4. Fluorescence of TiO_2:Cr^{3+} at 77 and 4 K. A_- and A_+ are no-phonon lines. The insert shows the splitting of the A_- line, which was recorded photographically.

the fluorescence, both the sharp line A_- and the broad band, is 45 μsec at 77 and 4 K. The broad-band emission and absorption are about twice as strong in σ as in π polarization. Table I lists the relative intensities of the various lines in σ and π polarization. From the σ, π, and α absorption spectra, we have determined that the sharp lines A_+ and A_- are magnetic dipole transitions and that the broad band is primarily of electric dipole character. The approximate oscillator strength for the lines A_+ and A_- is 4×10^{-8}, whereas that of the broad band is 3×10^{-4}. The linewidth of each of the two lines into which the line A_- splits (see inset of Fig. 4) is 0.6 cm^{-1} at 4 K. At 77 K these two lines coalesce into the single line A_- of width 16 cm^{-1}, a rather large increase.

A. $^4T_2$ or ^2E Excited State?

We first speculated that the lines A_+ and A_- originated from the $^2E_g \rightarrow {}^4A_{2g}$ transition of Cr^{3+}, commonly known as the R lines. However, the spectra we observe are uncharacteristic of the usual $^2E_g \rightarrow {}^4A_{2g}$ transition in the following respects.

(a) The lifetime of the Cr^{3+} fluorescence in TiO_2 is 45 μsec compared to the R-line lifetime of 4.3 msec in Al_2O_3,[17] 11.6 msec in MgO,[18] and 18.4 msec in $SrTiO_3$.[1] In fact, a lifetime of the order of milliseconds is characteristic of the $^2E_g \rightarrow {}^4A_{2g}$ transition of Cr^{3+} in any host.

(b) The phonon side bands of Cr^{3+} in TiO_2 have about 7×10^3 more integrated intensity than the zero-phonon lines. Normally, for Cr^{3+} in MgO or $SrTiO_3$ as examples, the ratio is of the order of 3:1.

(c) The peak intensity of the broad band occurs about 1000 cm^{-1} from the zero-phonon line and is structureless. This is indicative of multiphonon emission. Normally, R-line side bands consist of single lattice phonon creation; multiphonon creation is much weaker.

(d) The increase of linewidth of the zero-phonon line A_- from 0.6 cm^{-1} at 4 K to 16 cm^{-1} at 77 K is uncharacteristic of a $^2E_g \rightarrow {}^4A_{2g}$ transition.

TABLE I. Relative intensities of the zero-phonon lines.

	σ	π
Emission (77 K)		
A_+:A_-	1:3.6	1:2.3
Absorption (2 K)		
A_+:A_-	<1:5	1.1:1
Emission[a] (4 K)		
$A_-(m_s=\pm\frac{1}{2})$:A_- $(m_s=\pm\frac{3}{2})$	1.2:1	1.4:1

[a] The labels, $m_s=\pm\frac{1}{2}$ and $m_s=\pm\frac{3}{2}$ refer to the two components of the split $^4A_{2g}$ ground state. Gerritsen *et al.* found that the $m_s=\pm\frac{3}{2}$ state is lowest in energy.

As a typical counterexample, we cite Cr^{3+} in MgO and Al_2O_3, in which the width of the R lines hardly changes in going from 4 to 77 K.[17,19] Cr^{3++} in $SrTiO_3$ is exceptional, the linewidth increases by a factor of 8, but for good reason: The low-frequency transverse "optical" "soft mode" becomes populated above 30 K and causes a sizable contribution to the line broadening above the temperature. The lowest optical frequency of TiO_2, however, is ~140 cm^{-1}, which at 77 K is not appreciably populated.

We suggest that our observations on the infrared emission and absorption can be understood by assuming that the $^4T_{2g}$ state is the lowest-lying excited state and that we are dealing with transitions between this state and the $^4A_{2g}$ state of the Cr^{3+} ion. In support we offer points (a)–(b) mentioned above which are consistent with a $^4T_2 \rightarrow {}^4A_{2g}$ transition. Thus, the lifetime of 45 μsec is of the same order as that observed in Cr^{3+}-doped oxides, in which the lowest excited state has been established to be the $^4T_2$ state: $LiNbO_3$[5] (10 μsec), $LiTaO_3$[5] (11 μsec), and $ZnWO_4$[6] (10 μsec). Although a zero-phonon line has not been observed in the work cited above, for reasons we shall discuss later, a broad, almost structureless, band is observed in emission and absorption akin to our observations on Cr^{3+} in TiO_2. We also point to the large increase of the no-phonon linewidth, a factor of 25 in going from 4 to 77 K, as supporting our suggestion, since the $^4T_2$ state is more sensitive to crystal field than the ^2E state and, therefore, more sensitive to modulation by the electric field of phonons. Finally, we point out that the small value of the crystal-field parameter Dq = 1380 cm^{-1} in TiO_2 would favor the $^4T_2$ as the lowest excited state. This is to be compared with 1800 cm^{-1} (Al_2O_3), in which the ^2E state is lowest, and with 1550 cm^{-1} ($LiTaO_3$) and 1530 cm^{-1} ($LiNbO_3$), in which the $^2T_2$ state is the lowest excited state.

We reject the possibility that the emission originated from both states, the line emission from the ^2E state and the broad band from the $^4T_2$ state, on the ground that at 4 K emission would take place only from the lowest excited state. This, of course, is valid only if the energy transfer to the lowest excited state is rapid. That this is, indeed, the case is shown by our lifetime measurements which show the same lifetime of 45 μsec for the sharp line and broad-band emission. These facts are difficult to reconcile with an emission resulting from two distinct states.

B. $^4T_2$ State

The $^4T_2$ state consists of 12 components, which are labeled by products of orbital states, $|xz\rangle$, $|yz\rangle$, $|x^2-y^2\rangle$, and spin states, $m_s=-\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$. The coordinate system we are using is

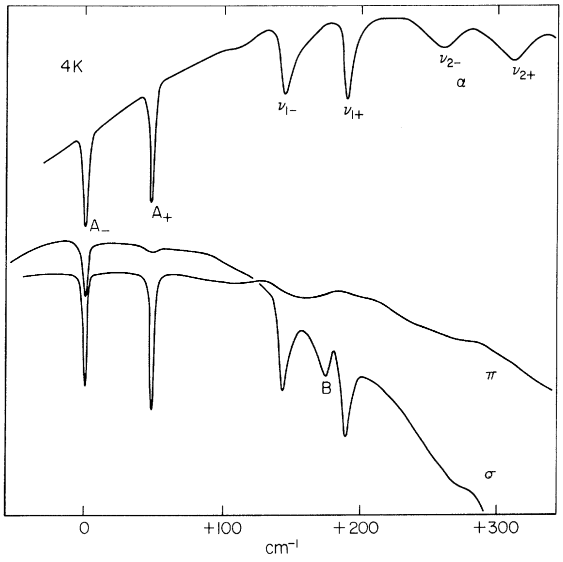

FIG. 5. Absorption spectrum of TiO_2:0.02% Cr at 4 K near the no-phonon transitions A_- and A_+ in α, π, and σ polarizations. The ordinate represents transmission. The curves are taken from actual experimental traces. ν_{1-}, ν_{1+}, and ν_{2-} and ν_{2+} are phonon side bands of the no-phonon lines A_- and A_+, respectively. The peak B which appears in the σ spectrum only and does not have a companion is proposed to be a third no-phonon $^4T_2 \rightleftharpoons {}^4A_2$ transition.

shown in Fig. 1. Because of the spin-orbit interaction and the orthorhombic (D_{2h}) site symmetry, the $^4T_2$ state is split into six Kramers doublets, all of symmetry Γ_5^+.[20] Since all six states have the same symmetry, there is complete mixing of the above-mentioned components. The energies and eigenfunctions of these six states cannot be obtained unless the magnitudes of the spin-orbit interaction and the orthorhombic fields are known.

We observe transitions to two of the six states, possibly a third. The existence of a third zero-phonon line is suggested by the results shown in Fig. 5. The peak B at $+172$ cm^{-1} from the A_- line appears only in the σ spectrum, indicating that it is a magnetic dipole transition. The 172-cm^{-1} peak also does not have a companion separated by 47 cm^{-1} as do all the other phonons in absorption. It is likely then that this line is a transition to a third state of the $^4T_2$ manifold.

It is possible to determine experimentally what the approximate eigenfunctions of these $^4T_2$ states might be. This can be done by knowing the intensities of the various transitions in the different polarizations. Table II lists the symmetries of the orbital components of $^4T_{2g}$ in D_{2h} symmetry along with the magnetic dipole selection rules. We also are fortunate to know the ground-state eigenfunctions from the EPR studies. Gerritsen *et al.*[4] find that the ground-state components are $m_s = \pm\frac{1}{2}$ and $m_s = \pm\frac{3}{2}$ with only a 3% admixture between the two due to the orthorhombic field. In principle, a careful measurement of the various line intensities in the different polarizations and use of the optical Zeeman effect could result in good eigenfunctions for these $^4T_2$ states. Thus, values for the spin-orbit coupling coefficient and the orthorhombic field could be obtained. For example, from Fig. 5 it can be seen that the A_- and A_+ lines are mainly π polarized. Thus, the two states associated with these transitions contain mostly the components $|xy\rangle$ or $|x^2-y^2\rangle$; whereas, the third line at $+172$ cm^{-1} appears only in the σ polarization and thus contains mostly $|yz\rangle$. However, a detailed study of this problem is beyond the scope of this paper.

C. Vibronics

Inspection of either the emission or absorption spectra shown in Fig. 3 and in greater detail in Figs. 4 and 6 shows two main characteristics of the vibronic spectra. These are first, a broad structureless phonon band peaking at 13 800 cm^{-1} in absorption and 11 700 cm^{-1} in emission, giving a Stokes shift of 2100 cm^{-1}; and second, phonon structure which differs in emission and absorption. These vibronic side bands are *not* typical of the cooperation of an electronic transition with unperturbed lattice phonons in which, characteristically, multiphonon cooperation is weaker than that of single phonons and in which the position of the phonon side bands with respect to the no-phonon line are mirror images of each other in absorption and emission. In addition, although the energies of the lattice phonon in TiO_2 are known for the center of the Brillouin zone,[11] normally a point with a large density of states, none of the peaks in the structure correspond to any of these phonons.

TABLE II. Symmetries and selection rules for the $^4T_2$–$^4A_2$ transitions in D_{2h} symmetry.

A. Symmetries in

	O_h	D_{2h}
T_{2g}:	$\vert xz\rangle$	Γ_2^+
	$\vert x^2-y^2\rangle$	Γ_1^+
	$\vert yz\rangle$	Γ_4^+
A_{2g}		Γ_3^+

B. Selection rules for magnetic dipole transitions (nonzero matrix elements)

$$\langle {}^4A_{2g} | M(x) | {}^4T_{2g}(xz)\rangle$$
$$\langle {}^4A_{2g} | M(y) | {}^4T_{2g}(yz)\rangle$$
$$\langle {}^4A_{2g} | M(z) | {}^4T_{2g}(x^2-y^2)\rangle ,$$

where M is the magnetic dipole moment operator, $M = \sum_i (l_i + 2S_i)$.

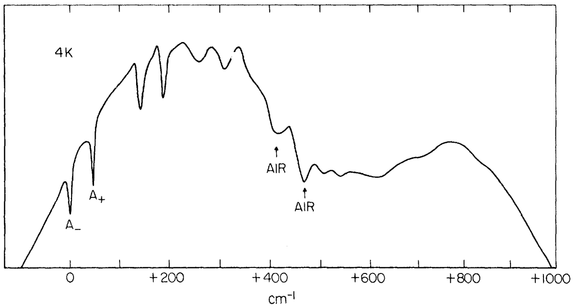

FIG. 6. α-absorption spectrum of TiO_2:0.005% Cr at 4 K. The ordinate represents transmission. These data complement those shown in Fig. 5 in which the Cr concentration is four times larger.

The above facts are further evidence against the zero-phonon lines being Cr^{3+} R lines which in emission have always shown lattice phonons.[1,2,19] In addition, in the case of ruby the phonon side bands of the R line in absorption and in emission are almost identical.[17] The reason this is the case for the R lines is that there is no "displacement recoil"[21] for the $^2E \rightarrow {}^4A_2$ transition, i.e., the equilibrium positions of the Cr ion and the surrounding nuclei are almost the same whether the Cr^{3+} ion is in the $^4A_2$ ground or the ^2E excited electronic state. Thus, no large relaxation to the new equilibrium position of the nuclei is necessary. Therefore, cooperation of phonons with the R line is described simply as a weak modulation of the $^4A_2$ and ^2E states by the normal mode displacements of lattice phonons. This type of interaction leads to phonon side bands for which the density of states of the lattice phonon states is the important factor in producing the side band shape.

The broad-band emission and absorption originating and terminating in the $^4T_2$ state is usually explained as due to a "displacement recoil," commonly displayed in a "configurational coordinate diagram." Because of the displacement recoil we do not expect an interaction with lattice phonons as simple as that observed for the R-line transition. In this case the Born-Oppenheimer approximation is used to separate the ion-lattice system into an electronic system and a lattice system. The energy and wave function of the electronic system depend parametrically on the position of the ion with respect to the lattice. The energy and wave functions of the lattice system, in turn, depend on the energy of the electronic system because the latter is shown to enter the lattice Hamiltonian as a potential energy. Consider the situation when a Cr^{3+} ion is substituted for a Ti^{4+} ion in TiO_2. In principle, we could calculate the phonon modes when the Cr^{3+} is in the $^4A_2$ ground and $^4T_2$ excited states, respectively. In each case, these modes include phonons which are not affected by Cr^{3+}, called lattice modes, and others which are perturbed to some extent, called defect modes, which include modes commonly labeled as localized, resonance, pseudolocalized, or band modes. The latter are generally different for the ^4A and $^4T_2$ states. At low temperatures, when no modes are excited, a transition of the Cr^{3+} ion from the $^4A_2$ to the $^4T_2$ state by the absorption of a photon excites the defect vibrational modes associated with the $^4T_2$ state and, in addition, the unperturbed lattice modes. In emission this is inverted in that the defect modes are associated with the $^4A_2$ state. Summarizing, the vibronic side bands consist of defect and lattice phonons. The defect phonons participating in absorption and emission are generally different.

Inspection of the phonon structure shows that none of the phonons in absorption match any of the phonons in emission. We, therefore, conclude that the vibronic side bands are principally composed of defect modes and that participation by lattice phonons occurs only in combination with defect modes.

In this paragraph, we comment on the interesting experimental fact that the vibronic side bands are principally electric dipole transitions. We first remark that the no-phonon transition has magnetic dipole character. Therefore, in the "Condon approximation," which neglects the dependence of the "electronic" part of the total wave function on the phonon coordinates, side bands of electric dipole character are not allowed. Furthermore, the site symmetry of Cr^{3+} must contain inversion when the Cr^{3+} is in the $^4T_2$ or $^4A_2$ state. Therefore, (a) the defect modes can be separated into even and odd modes. The same separation, of course, can be made for the lattice modes. (b) The "displacement recoil" associated with the $^4A_2 \rightleftarrows {}^4T_2$ transition is necessarily of even symmetry. We thus expect the phonon side bands to contain even phonons.

In going beyond the Condon approximation, we can expand the electronic wave function to first order in the odd phonon coordinates (the even phonon coordinates do not contribute). In this approximation, it can be shown[22] that electric dipole transitions involving multiphonon emission are allowed in which many even phonons but only one odd phonon participate. To this, of course, must be added the contribution due to the magnetic dipole moment connecting the even-phonon states. The latter contribution, however, is expected to be small compared to the former. Expansion of the electronic wave function to orders higher than first order in the phonon coordinates can be shown

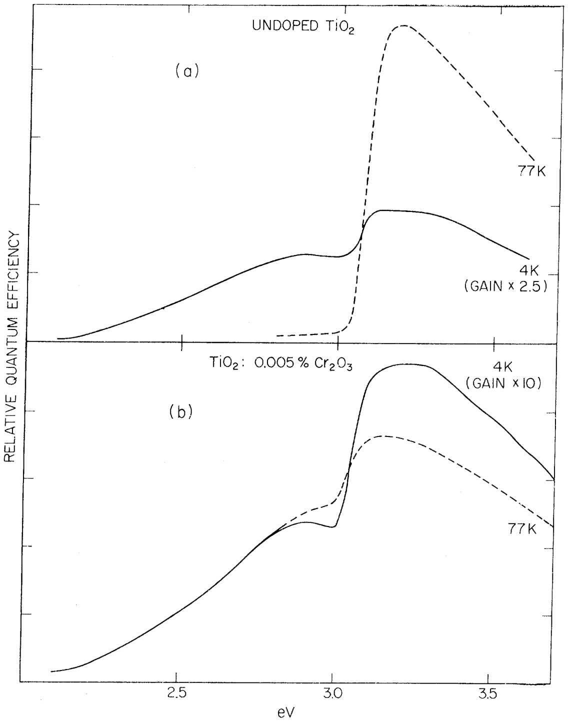

FIG. 7. Excitation spectra of the infrared fluorescence in (a) undoped TiO_2, and (b) TiO_2:Cr^{3+} at 4 and 77 K.

to lead to electric dipole transitions involving odd phonons, the number of which depend on the order of the expansion, In addition, as in the case of the first-order expansion, many even phonons participate. Nevertheless, we expect the first-order term to dominate because the "displacement recoil" is of even symmetry. Summarizing, we conclude that the vibronic side bands are mainly composed of even phonons "assisted" by a single odd phonon.

The inversion of the experimental results on such vibronic side bands to obtain quantitative information about the dynamical properties of the Cr^{3+} ion or the TiO_2 lattice is a formidable problem[23] and we restrict ourselves to the qualitative remarks made above. We call attention to recent theoretical work which deals with the problem of phonon cooperation in an optical transition, by these localized or lattice phonons, from a unified point of view.[22,24]

We finally would like to point to the connection of this work with previous work. McClure,[25] in his study of the optical spectra of transition-metal ions in Al_2O_3, discusses the absorption spectrum of the ${}^4A \rightarrow {}^4T_2$ transition of Cr^{3+}. The general features of the absorption spectrum are similar to those of Cr^{3+} in TiO_2. In Al_2O_3 the no-phonon line is much wider, presumably because of lifetime broadening since the ${}^4T_2$ state is not the lowest-lying excited state. Glass's[5] study of the spectra of Cr^{3+} in $LiNbO_3$ and $LiTaO_3$ also seems relevant. In these materials the ${}^4T_2$ state is identified as the lowest-lying excited state; however, the zero-phonon line of the ${}^4T_2 \rightarrow {}^4A_2$ transition is not seen in absorption or emission. The reason for this is the lack of overlap of the zeroth vibrational states of the ${}^4A$ and ${}^4T_2$ states which are moved to nonoverlapping regions of configuration space by the large Stokes shift 4600 cm^{-1} and 5000 cm^{-1} in $LiNbO_3$ and $LiTaO_3$, respectively. In TiO_2 by comparison we find a Stokes shift of 2100 cm^{-1}. In emission, Glass finds two lines as precursors to a broad structureless band. He concludes that these lines are not zero-phonon lines of the ${}^4T_2 \rightarrow {}^4A_2$ transition. We suggest that they may be structures due to defect phonon participation.

IV. EXCITATION SPECTRUM

Figure 7 shows the excitation spectrum of the total emission, i.e., no-phonon line plus the vibronics. The excitation spectrum of the no-phonon line was found to be identical. This confirms the conclusion, already made from the identity of the lifetime of the no-phonon and vibronic emission, that the Cr^{3+} emission originates from a single state. A comparison of the excitation spectrum with the gross absorption spectrum of TiO_2: 0.005% Cr shown in Fig. 2 shows that the "background absorption" previously referred to is duplicated in the excitation spectrum. In addition, however, the excitation spectrum shows an increase in excitation at photon energies at which free charge carriers are produced (~3 eV). This is shown by a comparison of the excitation spectrum with the spectral response of photoconductivity shown in Fig. 8. From this, we conclude that the excitation of the Cr^{3+} ions is derived mainly from "traps" which are filled by charge carriers, rather than from the direct excitation of the Cr^{3+} ion, in contrast to Cr^{3+} in Al_2O_3 and MgO, for example.

These experimental facts are duplicated in the case of Cr^{3+} in $SrTiO_3$.[1,2] We think that the conclusions drawn above apply equally to $SrTiO_3$ and that those drawn by one of us (L.G.) are incorrect. The latter assumed with Müller[26] that the absorption bands observed in Cr-doped $SrTiO_3$ are the ${}^4A_2 \rightarrow {}^4T_2$ and ${}^4A_2 \rightarrow {}^4T_1$ of the Cr^{3+} ions, respectively. In fact, they are principally "background absorption," as in TiO_2, due to some unknown defect, as concluded by Stokowski and Schawlow.[1]

V. SUMMARY

In this paper, we began by noting that, optically,

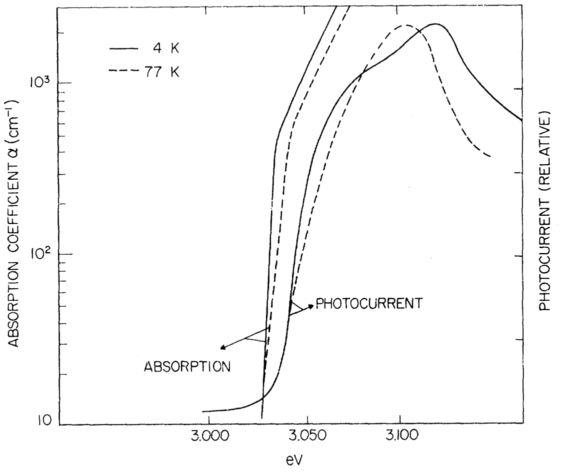

FIG. 8. Photoconductivity of undoped TiO_2 at 4 and 77 K, respectively. The *K* vector of the incident radiation is parallel to the *c* axis. The absorption spectrum is reproduced from D. C. Cronemeyer [Phys. Rev. 87, 876 (1952)].

Cr-doped TiO_2 shows the same ground-state splitting observed by others in EPR, and identified there as Cr^{3+} substituting for Ti^{4+}. We thus conclude that the no-phonon lines observed in absorption and emission are due to Cr^{3+}. We next seek to identify the excited states involved and remark that the spectra observed do not appear to be characteristic of the "usual" $^4A_2 \rightleftharpoons {}^2E_2$ transitions. Next, we reject the possibility that the spectra are due to transitions between several, rather than just two, electronic states. We then speculate that the lowest excited state of Cr^{3+} in TiO_2 is the $^4T_2$ rather than the usual ^2E state and conclude by listing evidence for this hypothesis.

If the lowest excited electronic state of Cr^{3+} is, indeed, the $^4T_2$ state, it is unique in yielding a no-phonon line. Moreover, it is noteworthy that the participating phonon states are impurity modes and that these are different for the $^4T_2$ and the $^4A_2$ electronic states.

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